

Structure Analysis of Diamond-like Carbon Films by NEXAFS

Kwang Yong Eun¹, Kwang-Ryeol Lee¹, Simone Anders² and Thomas Stammer²

¹Thin Film Technology Research Center, Korea Institute of Science and Technology,
P.O. Box 131, Cheongryang, Seoul, 130-650, Korea

²Advanced Light Source, Ernest Orlando Lawrence Berkeley National Laboratory,
University of California, Berkeley, CA, 94720, USA

INTRODUCTION

The economical and technological properties of diamond-like carbon (DLC) films have attracted the interest of many researchers [1-5]. DLC films exhibit excellent properties regarding hardness, electrical insulation, chemical inertness, optical transparency, surface smoothness, resistance to wear, and electron emission.

For the deposition of hydrogenated DLC films, the r.f. plasma CVD process is one of the well established methods and the properties of the films can vary depending on the process parameters such as bias voltage, precursor gas, gas pressure, and so on [1-5]. Among these variables, the bias voltage shows the most significant effect on the mechanical, optical, and electrical properties. This means that bias voltage change results in a structure variation of DLC films during deposition.

The bias voltage is strongly related to the mean ion energy during CVD deposition. It is very important to measure the sp^2 and sp^3 composition in the DLC films since the properties are clearly dependent upon the sp^2/sp^3 ratio. In order to evaluate the ratio of sp^2 and sp^3 in the Raman spectra of DLC films, the graphic separation of individual peaks is needed for the complicated broad peak between 1300 and 1600 cm^{-1} , and this allows only qualitative analysis. On the other hand, the π^* resonance peak at 285 eV in the K-edge carbon NEXAFS spectra is very sharp and is very sensitive to the sp^2 fraction [6-8]. For the basic study of the structure of the hydrogenated DLC films, different samples were prepared by varying bias voltage, and NEXAFS analysis was performed for the quantitative analysis of the sp^2 and sp^3 ratio, and consequently for the better understanding of the properties of the films.

EXPERIMENTAL

DLC films were synthesized on silicon (001) wafers by r.f. plasma CVD at a pressure of 10 mTorr. Precursor gas was benzene and bias voltage was varied from -100 to -700 volt. Details of experimental set-up was described elsewhere [9]. The deposited thickness of all DLC films was 1 μm . The NEXAFS measurements were performed at the photo-emission electron microscope situated at the undulator beam-line 8.0 of the ALS. Beam intensity was carefully controlled at a low level.

RESULTS and DISCUSSION

The properties of deposited DLC films showed monotoneous increasing or decreasing trend with increase of bias voltage applied. Hydrogen content decreased from 30% to 22%, and the hardness and residual stress of the films increased from 1500 to 1800 $kg\ mm^{-2}$ and from 0.5 to 1.8 GPa respectively with increase of the bias voltage. This property variation is known to be dependent on the ion energy which is proportional to Vb/\sqrt{P} where Vb is bias voltage and P is gas pressure [5]. The properties should be dependent upon the bias voltage since the pressure was kept constant.

The NEXAFS plots of the DLC films showed clear decreasing trend of graphite peak height in 285 eV with increase of bias voltage as shown in Fig. 1.

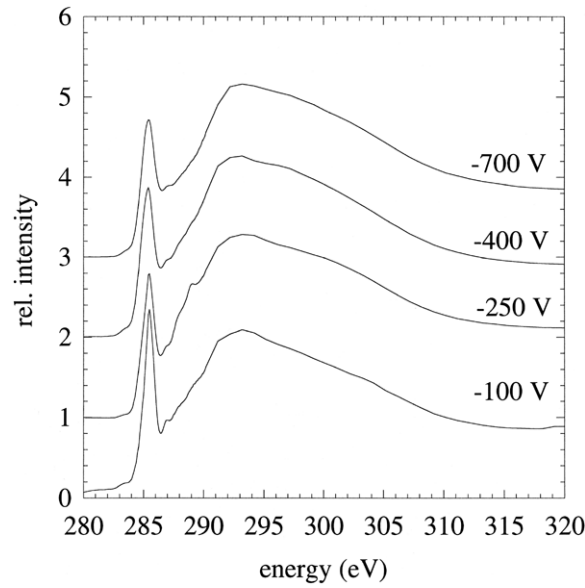


Fig.1. Carbon K-edge NEXAFS spectra of DLC films deposited with different bias voltage from -100 volt to -700 volt .

There are very small peaks between 286.5 eV and 290 eV. The small peak at around 287 eV shows decreasing trend with increase of bias voltage. This is consistent to the decreasing trend of the hydrogen content in the films. This hydrogen peak height is so low that the amount of C-H bond seems to be not so high comparing the sp^2 and sp^3 bond. The curves at energies higher than 320 eV were very flat as in Fig.1 and this constant value is known to be proportional to the total carbon amount in the films [10]. The film deposited at -250 bias voltage shows a particular peak at 289 eV and a higher value in the flat curve for energies higher than the 315 eV. The reason for this is not clear yet.

The sp^3 component can be calculated by the equation $1 - \{(sp^2 - T_c)/T_c\}$ where sp^2 is the peak height of the π^* resonance at 285 eV and T_c is the height of the flat part above 320 eV, neglecting the hydrogen component [10]. Fig.2 shows the calculated sp^3 fraction plot depending on the bias voltage variation.

The sp^3 component in the DLC films increased significantly with increase of the bias voltage as shown in Fig.2, and this increasing trend of the diamond bond component is consistent to the same increasing trend of the hardness and the residual stress in the films. The radiation damage of the x-ray synchrotron might give some errors in the sp^2 peak height. The confirmation of the sp^2 and sp^3 composition in the DLC films by EELS analysis is required to evaluate the error ranges. Further study is needed for the composition variety of DLC films and the standardization of the quantitative analysis results.

CONCLUSION

The hydrogenated DLC films with different composition were obtained by the bias voltage variation from -100 to -700 volt during the r.f. plasma CVD synthesis. The sp^2 peak showed a

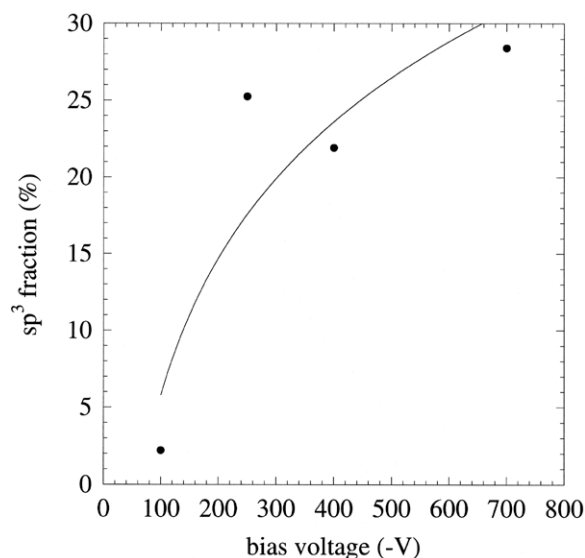


Fig.2. Calculated sp^3 fraction variation in the hydrogenated DLC films depending on the applied bias voltage during the r.f. plasma CVD synthesis

clear decreasing trend with the increase of the applied bias voltage. The sp^3 composition of each film was derived from the calculation of the sp^2 composition by the normalization and fractionalizing the total carbon content measured from the flat value above the 320 eV. The increasing trend of the calculated sp^3 composition in the DLC films with increase of the bias voltage was consistent with the increasing trend of the hardness and residual stress depending on the same variation.

REFERENCES

1. C. Wild, J. Wagner, P. Koidl, J. Vac. Sci. Technol. A, 5, 2227 (1987)
2. X. Jiang, J. W. Zou, K. Reichelt, P. Grunberg, J. Appl. Phys., 66, 4729 (1989)
3. J. Robertson, Surf. Coat. Technol., 50, 185 (1992)
4. A. Grill, V. Patel, Diamond Relat. Mater., 2, 1519 (1993)
5. K.-R. Lee, Y.-J. Baik, K. Y. Eun, Diamond Relat. Mater., 3, 1230 (1994)
6. G. Comelli, J. Stor, C. J. Robinson, W. Jark, Phys. Rev. B 38, 7511 (1988)
7. A. Gutierrez, J. Diaz, M. F. Lopez, Appl. Phys. A, 61, 111 (1995)
8. M. Jaouen, G. Tourillon, J. Delafond, N. Junqua, G. Hug, Diamond Relat. Mater., 4, 200 (1995)
9. K.-R. Lee, Y.-J. Baik, K. Y. Eun, Diamond Relat. Mater., 2, 218 (1993)
10. S. Anders, Unpublished Data on the sp^2 and sp^3 ratio of a-C

This research was supported by the Laboratory Technology Research Partnership Program, Office of Energy Research, U.S. Department of Energy under a CRADA (Cooperative Research and Development Agreement) between Lawrence Berkeley National Laboratory and IBM; and by the Director, Office of Energy Research, Office of Basic Energy Sciences, under U.S. DOE Contract DE-AC03-76SF00098.

Principal investigator: Simone Anders, Berkeley Lab. Email: sanders@lbl.gov. Telephone: 510-486-5928.